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Applicant : Matsushita Electric Industrial Co., Ltd.

DECLARATION

I, Masamichi Matsuda

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am the translator of the attached documents and certify that the following is a true
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This is April 6, 2007

A handwritten signature in black ink, appearing to read "M. Matsuda", written over a horizontal line.

MASAMICHI MATSUDA



(Translation)

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[Document Name] Specification

[Title of the Invention]

ELECTRODE OF POLYMER ELECTROLYTE TYPE FUEL CELL
AND METHOD OF PRODUCING THE SAME

[Scope of Claims]

[Claim 1] An electrode of a polymer electrolyte type fuel cell, being provided on a one side or both sides of a polymer electrolyte membrane, and containing at least a finely divided carbon powder having a noble metal catalyst supported thereon,

 wherein said electrode contains at least a catalyst layer and a gas diffusion layer, and the volume resistivity of said catalyst layer is not greater than 100 ($\Omega \cdot \text{cm}$).

[Claim 2] A method of producing an electrode of a polymer electrolyte type fuel cell being provided on a one side or both sides of a polymer electrolyte membrane, and containing at least a finely divided carbon powder having a noble metal catalyst,

 wherein said electrode contains at least a catalyst layer and a gas diffusion layer, and

 said catalyst layer is formed by spreading a paste containing said finely divided carbon powder having a noble metal catalyst supported thereon, over a predetermined support and drying the coated support, and the volume resistivity of said catalyst layer is not greater than

100 ($\Omega \cdot \text{cm}$).

[Claim 3] An electrode of a polymer electrolyte type fuel cell, being provided on a one side or both sides of a polymer electrolyte membrane, and containing at least a finely divided carbon powder having a noble metal catalyst supported thereon,

wherein said electrode contains at least a catalyst layer and a gas diffusion layer, and

the ratio of the volume resistivity of said catalyst layer to the volume resistivity of said gas diffusion layer (volume resistivity of catalyst/volume resistivity of gas diffusion layer) is not greater than 10^7 .

[Claim 4] A method of producing an electrode of a polymer electrolyte type fuel cell being provided on a one side or both sides of a polymer electrolyte membrane, and containing at least a finely divided carbon powder having a noble metal catalyst,

wherein said electrode contains at least a catalyst layer and a gas diffusion layer,

said catalyst layer is formed by spreading a paste containing said finely divided carbon powder having a noble metal catalyst supported thereon, over a predetermined support and drying the coated support, and the ratio of the volume resistivity of said catalyst layer to the volume resistivity of said gas diffusion layer (volume resistivity

of catalyst/volume resistivity of gas diffusion layer) is not greater than 10^7 .

[Claim 5] An electrode of a polymer electrolyte type fuel cell according to Claim 1 or 3, wherein the volume resistivity of said catalyst layer is not greater than $20 (\Omega \cdot \text{cm})$.

[Claim 6] A method of producing an electrode of a polymer electrolyte type fuel cell according to Claim 2 or 4, wherein the volume resistivity of said catalyst layer is not greater than $20 (\Omega \cdot \text{cm})$.

[Detailed Description of the Invention]

[0001]

The present invention relates to an electrode of a polymer electrolyte type fuel cell and a method of producing the electrode which is provided on a one side or both sides of a polymer electrolyte membrane, and has at least a catalyst layer containing at least a finely divided carbon powder having a noble metal catalyst supported thereon.,

[0002]

[Prior Art]

A fuel cell allows the electrochemical reaction of a fuel gas with an oxidizer gas containing oxygen such as air to generate electric power energy. A polymer electrolyte type fuel cell is a kind of fuel cell. An

example of single cell constituting a polymer electrolyte type fuel cell is shown in Fig. 1.

[0003]

In Fig. 1, the reference numeral 1 indicates a polymer membrane which is used as a hydrogen ionically-conductive membrane. The reference numeral 2 indicates a fuel electrode formed by a gas diffusion layer comprising a carbon sheet and a water-repellent layer and a catalyst layer. The reference numeral 3 indicates an air electrode formed by a gas diffusion layer and a catalyst layer which are similar to the fuel electrode cell. The reference numeral 5 indicates a separator which acts to prevent the mixing of hydrogen supplied onto the fuel electrode and air supplied onto the air electrode in the assembly of fuel cell having single cells bonded to each other.

[0004]

This polymer electrolyte type fuel cell is prepared as follows. Firstly, a carbon powder having a noble metal catalyst supported thereon (hereinafter referred to as "catalyst-supporting carbon powder") as a catalyst body is mixed with a binder resin to prepare a catalyst layer paste. Further, a gas diffusion layer is formed by, e.g., a carbon paper having both permeability to fuel gas containing hydrogen and electronic conductivity which has been subjected to water repellent treatment. The

aforementioned paste is then spread over the gas diffusion layer to form a catalyst layer thereon, thereby preparing an electrode (Therefore, the step of preparing a paste is occasionally referred to as "step of preparing a coating compound").

In order to render this catalyst layer smooth and free of agglomerate, it is necessary that the paste be subjected to mixing at a high shear rate to accelerate the formation of the catalyst-supporting carbon powder into primary particles.

[0005]

Subsequently, this electrode is bonded to one or both sides of a polymer electrolyte membrane which selectively transports hydrogen ion to prepare a single cell. As the polymer electrolyte membrane there is normally used a perfluorosulfonic acid which is a hydrogen ionically-conductive polymer electrolyte.

[0006]

The aforementioned binding resin is adopted to enhance the bond properties of the catalyst layer with the gas diffusion layer and the polymer electrolyte membrane. As the binder resin there is normally used a perfluorosulfonic acid as in the case of polymer electrolyte membrane.

[0007]

In order to further enhance the bond properties, as a binder resin there is also incorporated a fluororesin such as polytetrafluoroethylene and polyvinylidene fluoride.

[0008]

However, since the catalyst-supporting carbon powder is a particulate material comprising primary particles having a diameter of not greater than 100 nm and thus tends to undergo agglomeration, the particles remain primary shortly after mixed at a high shear rate but undergo agglomeration with the evaporation of the solvent during spreading and drying, sometimes resulting in the a catalyst layer occurrence of pinholes or cracking in the catalyst layer portion.

[0009]

In a fuel cell having such a catalyst layer, such cracking sometimes causes the occurrence of current density distribution that deteriorates the discharge performance or the catalyst layer falls off the cracked area, deteriorating the life performance of the cell.

[0010]

[Problems to Solve the Invention]

An aim of the present invention is to provide an electrode of a polymer electrolyte type fuel cell and method of producing the quality electrode which can solve the

problems as described above with no leak and improved life performance.

[0011]

[Means to Solve the Problems]

To solve the above problems, the inventors studied the relationship between the properties of electrode coat layer and the discharge performance. As a result, the measurement of the volume resistivity of the catalyst layer shows that electrodes having much area of pinholes or cracking exhibit a high volume resistivity while electrodes free of pinholes or cracking exhibit a low volume resistivity. It was also found that a fuel cell comprising an electrode having a low volume resistivity undergoes no leak and thus provides a polymer electrolyte type fuel cell having improved life performance.

[0012]

In an electrode of a polymer electrolyte type fuel cell and a method of producing the electrode of the present invention, a catalyst-supporting carbon powder having a catalyst supported thereon as a catalyst body is mixed with solvent and a binder resin to prepare a catalyst layer paste. Then, in the step of spreading the paste to a base material having conducting properties and drying it, the electrode is produced so that the volume resistivity of the catalyst layer is not greater than 100 ($\Omega \cdot \text{cm}$).

[0013]

Further, the electrode is produced so that the ratio of the volume resistivity of said catalyst layer to the volume resistivity of said gas diffusion layer (volume resistivity of catalyst/volume resistivity of gas diffusion layer) is not greater than 10^7 . Then, the electrode is bonded to both sides of a polymer electrolyte membrane to prepare a single cell.

[0014]

[Embodiments]

Embodiments of implementation of the present invention will be described hereinafter.

[0015]

As the carbon powder having a platinum group noble metal supported thereon there may be used an electrically-conductive carbon black such as ketjen black and acetylene black.

[0016]

As the binder resin there is normally used a perfluorosulfonic acid which exerts an effect as a hydrogen ionically-conductive polymer electrolyte. Moreover, for the purpose of enhancing bond properties, a fluororesin such as polytetrafluoroethylene, polyvinylidene fluoride resin and polyvinylidene fluoride-hexafluoropropylene copolymer may be used as a binder resin. Further, a

treatment may be previously conducted to cause a fluoro-resin to be attached to a carbon powder having a noble metal supported thereon using a mixer such as Henschel mixer produced by MITSUI MINING COMPANY, LIMITED.

[0017]

As solvents to be mixed with the carbon powder having a noble metal supported thereon there may be used water, ethyl alcohol, methyl alcohol, isopropyl alcohol, ethylene glycol, methylene glycol, propylene glycol, methyl ethyl ketone, acetone, toluene, xylene, n-methyl-2-pyrrolidone, etc., singly or in combination of two or more thereof. The amount of these solvents to be added is preferably from 10 to 400 based on 100 of the catalyst powder by weight.

[0018]

Referring to the method of preparing the catalyst layer paste, a carbon powder having a catalyst supported thereon, a binder resin and optionally solvents may be processed by facilities such as disolver, double planetary mixer, kneader, bead mill, ultrasonic dispersion machine and ultrahigh pressure homogenizer, singly or continuously in succession, to prepare the catalyst layer paste.

[0019]

Referring to the method of spreading the catalyst layer paste, facilities such as comma coater, kiss coater, roll coater, doctor blade, spray coater, die coater and

gravure coater may be used. As drying means there may be used infrared drying, hot air drying or UV curing drying method.

[0020]

The volume resistivity of the catalyst layer thus spread and dried is preferably not greater than $100 [\Omega \cdot \text{cm}]$. It can be seen that when the volume resistivity is greater than $100 [\Omega \cdot \text{cm}]$, the resulting electrode is much provided with so-called cracking or pinholes and thus is not provided with discharge performance.

[0021]

The lower limit of the volume resistivity is preferably low. However, since the volume resistivity of the simple body of the carbon having a catalyst supported thereon to be used in the catalyst layer is $10^{-3} [\Omega \cdot \text{cm}]$, the lower limit of the volume resistivity of the catalyst layer is substantially $10^{-3} [\Omega \cdot \text{cm}]$ and it cannot be substantially anticipated that the lower limit of the volume resistivity of the catalyst layer falls below this value.

Referring to the method of predetermining the volume resistivity of the electrode thus spread and dried to be not greater than $100 [\Omega \cdot \text{cm}]$, various kinds of methods are possible, thus it is not necessary to restrict methods in particular.

[0022]

For example, the drying rate of the catalyst paste may be reduced so that the catalyst paste is dried without causing cracking in the catalyst layer. For example, a method can be proposed which comprises optimizing the drying temperature and amount of air flow in the hot air dryer. Alternatively, a method may be used which comprises preparing a solvent mixture having a stepwise combination of boiling points of various solvents.

[0023]

The gas diffusion layer can be formed by mixing acetylene black as a carbon powder with an aqueous dispersion of a polytetrafluoroethylene, spreading the ink over a carbon paper which acts as a base material of gas diffusion layer, and then subjecting the coated material to heat treatment. During this procedure, the volume resistivity of the gas diffusion layer can be controlled by the kind of carbon paper which acts as a base material and the amount of acetylene black to be incorporated. The ratio of the volume resistivity of the aforementioned catalyst layer to the volume resistivity of the aforementioned gas diffusion layer (volume resistivity of catalyst/volume resistivity of gas diffusion layer) is preferably not greater than 10^7 . When the ratio of the volume resistivity of the aforementioned

catalyst layer to the volume resistivity of the aforementioned gas diffusion layer exceeds 10^7 , the resistivity of the catalyst layer to the gas diffusion layer changes greatly, causing the drop of discharge efficiency.

[0024]

In other words, the lower limit of the volume resistivity ratio is not specifically limited. However, since the volume resistivity of the carbon paper to be used in the gas diffusion layer is about 10^{-5} [$\Omega \cdot \text{cm}$], it is substantially difficult to predetermine the lower limit of the volume resistivity of the gas diffusion layer to be not greater than this value. The lower limit of the volume resistivity of the gas diffusion layer is normally from 10^{-5} to 10^{-3} [$\Omega \cdot \text{cm}$].

The method of predetermining the ratio of the volume resistivity of the catalyst layer to the gas diffusion layer to be not greater than 10^7 is not specifically limited, but the drying rate of the catalyst paste may be reduced so that the catalyst paste is dried without causing cracking as mentioned above with reference to the method of preparing the catalyst layer. For example, a method can be proposed which comprises optimizing the drying temperature and amount of air flow in the hot air dryer. Alternatively, a method may be used which comprises preparing a solvent

mixture having a stepwise combination of boiling points of various solvents.

These methods may be combined with a method which comprises spreading a catalyst layer paste over a gas diffusion layer, and then drying the coated material, a method which comprises spreading a catalyst layer over a polymer support such as polypropylene and polyethylene terephthalate, drying the coated material, and then subjecting the coated material to hot press to cause transfer, a method which comprises directly spreading a catalyst layer paste over a polymer membrane, drying the coated material, and then laminating the coated material on a gas diffusion layer or the like to make accomplishment.

[0025]

(Example)

Examples of the present invention will be described hereinafter.

[0026]

(Example 1)

Referring to a first embodiment of implementation of the present invention, a step of preparing a coating compound of catalyst layer was carried out by mixing a catalyst-supporting carbon powder having 50% by weight of platinum catalyst supported on ketjen black which is a carbon powder with a composition of 1/1/1 mixture of

water, isopropyl alcohol and ethylene glycol as a solvent using a 20 l mixer produced by TOKUSHU KIKI KOGYO CO., LTD., and then mixing the mixture with a perfluorosulfonic acid as a hydrogen ionically-conductive agent and binder in an amount of 10% based on the carbon component of the carbon powder having a catalyst supported thereon to prepare an anode paste having a solid content concentration of 20 wt%.

[0027]

Next, a method of producing a gas diffusion layer will be described. Acetylene black which is a carbon powder was mixed with an aqueous dispersion of a polytetrafluoroethylene to prepare a water-repellent ink containing a polytetrafluoroethylene in a dried amount of 20% by weight. This ink was spread over a carbon paper which acts as a base material of gas diffusion layer so that it penetrated the carbon paper, and then was subjected to heat treatment at 300°C using a hot air dryer to form a gas diffusion layer.

[0028]

Subsequently, the aforementioned catalyst ink was spread over the aforementioned gas diffusion layer, and then dried at 80°C in a drying oven to form a catalyst layer. The catalyst layer was then bonded to both sides of a polymer electrolyte membrane to prepare an electrode.

[0029]

Subsequently, a gasket plate made of rubber was bonded to the polymer electrolyte membrane of the electrode thus prepared on the periphery thereof. A manifold hole for the passage of cooling water, fuel gas and oxidizer gas was then formed.

[0030]

Subsequently, two sheets of electrically-conductive separators, which have a gas passage and a cooling water passage, made of graphite sheet impregnated with a phenolic resin were used. A separator having an oxidizer gas passage formed thereon was laminated on one side of another electrode. A separator having a fuel gas passage formed thereon was laminated on the other side of the electrode to obtain a single cell as shown in Fig. 1.

[0031]

(Example 2)

A fuel cell was prepared in the same manner as in Example 1 except that a composition is a 1/2/3 mixture of water, isopropyl alcohol and ethylene glycol as a solvent in the catalyst paste.

[0032]

(Example 3)

A fuel cell was prepared in the same manner as in Example 1 except that the catalyst layer is formed by

spreading a catalyst paste over a polymer membrane and drying the coated material, and is bonded to the gas diffusion layer on both sides.

[0033]

(Comparative Example 1)

A fuel cell was prepared in the same manner as in Example 1 except that the catalyst layer is formed at 120 °C as a condition of drying a coated membrane.

[0034]

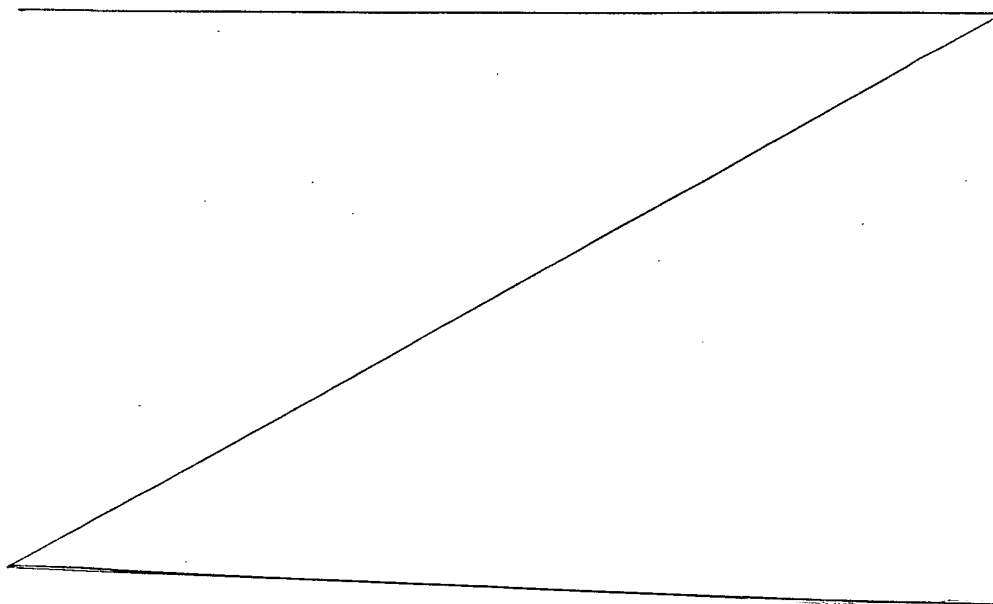
(Comparative Example 2)

A fuel cell was prepared in the same manner as in Example 1 except that the catalyst layer is formed with 100% of ethanol as the solvent of the catalyst layer.

[0035]

Conditions of production of catalyst electrode will be set forth in Table 1.

[0036]



【TABLE. 1】

| | Example 1 | Example 2 | Example 3 | Comparative Example 1 | Comparative Example 2 |
|-----------------------------------|---|---|---|---|----------------------------------|
| Catalyst layer solvent | Water/IPA/ Ethylene glycol =1/1/1 | Water/IPA/ Ethylene glycol =1/2/3 | Water/IPA/ Ethylene glycol =1/1/1 | Water/IPA/ Ethylene glycol =1/1/1 | Ethanol =100% |
| Catalyst layer drying temperature | 80°C | 80°C | 80°C | 120°C | 80°C |
| Catalyst layer forming method | Spreading on gas diffusion layer | Spreading on gas diffusion layer | Spreading on polymer membrane | Spreading on gas diffusion layer | Spreading on gas diffusion layer |

The electrodes and single cells thus obtained were evaluated for the following properties.

(1) Cracking on electrode

The electrode was subjected to segmentation to determine cracking occupation area.

(2) Electrode volume resistivity

The electrode was measured by a resistivity meter to calculate volume resistivity.

(3) Discharge rate, life performance

The cell was subjected to discharge test at a cell temperature of 75°C, a fuel gas utilization rate (U_f) of 70% and an air utilization ratio (U_o) of 40% with a pure hydrogen gas and air supplied onto the fuel electrode and the air electrode, respectively, and the gas moistening being conducted by passing the fuel gas through a bubbler at 70°C and air through a bubbler at 50°C.

[0037]

Fig. 2 illustrates examples of current-voltage characteristics of hydrogen-air type fuel cells of the examples of the present invention and the comparative examples. The data of discharge rate were evaluated with % relative to the voltage at 0.7mA/cm² of comparative examples.

[0038]

Fig. 3 illustrates examples of the life performance

of these cells. The life performance is evaluated with % relative to the voltage after 5000 hrs of comparative examples.

[0039]

Table 2 shows the results of evaluation of the electrodes and cells.

[0040]

[TABLE. 2]

| | Example 1 | Example 2 | Example 3 | Comparative Example 1 | Comparative Example 2 |
|---------------------------------------|---------------------------------|---------------------------------|---------------------------------|----------------------------------|----------------------------------|
| Cracking occupation area on electrode | 12% | 12% | 20% | 25% | 30% |
| Volume resistivity | 10 [$\Omega \cdot \text{cm}$] | 15 [$\Omega \cdot \text{cm}$] | 20 [$\Omega \cdot \text{cm}$] | 120 [$\Omega \cdot \text{cm}$] | 180 [$\Omega \cdot \text{cm}$] |
| Discharge rate (100% in Example 1) | 100% | 100% | 98% | 90% | 88% |
| Life performance (100% in Example 1) | 100% | 102% | 102% | 92% | 80% |

As can be seen in the results, the cracking is preferably less than 25%.

[0041]

The requirement that the ratio of the volume resistivity of the aforementioned catalyst layer to the volume resistivity of the aforementioned gas diffusion layer (volume resistivity of catalyst/volume resistivity of gas diffusion layer) is preferably not greater than 10^7 can be easily derived from the fact that the aforementioned catalyst volume resistivity is preferably 100 [$\Omega \cdot \text{cm}$] and the fact that the volume resistivity of the gas diffusion layer is from 10^{-5} to 10^{-3} [$\Omega \cdot \text{cm}$].

[0042]

The embodiments of implementation of the present invention have been described with reference to the method of producing an anode catalyst layer of fuel cell. However, similar results were obtained with cathode catalyst layer.

Industrial Applicability

[0043]

[Effect of the Invention]

As can be seen in the description given above, the present invention can provide an electrode of a high quality polymer electrolyte type fuel cell which undergoes no leak and exhibits an improved life performance and a method of producing the electrode.

[Brief Description of the Drawings]

[Fig. 1]

Fig. 1 is a sectional view illustrating the outline of the configuration of a single cell which is a constituent of an ordinary fuel cell stack.

[Fig. 2]

Fig. 2 is a current density- voltage characteristics graph of the cell of Example of the present invention.

[Fig. 3]

Fig. 3 is a current density- life performance graph of the cell of Example of the present invention.

(Description of Reference Numerals)

1. Polymer membrane
2. Air electrode
- 3 Fuel electrode
4. Separator
5. Separator

[Document Name] Abstract of Disclosure

[Abstract]

[Object]

In conventional polar plates, it was found that electrodes having much area of pinholes or cracking exhibit in a catalyst layer have many leaks and short life performance, and a cell comprising a catalyst layer having no pinholes or cracking exhibits undergoes no leak and have improved life performance.

[Solution]

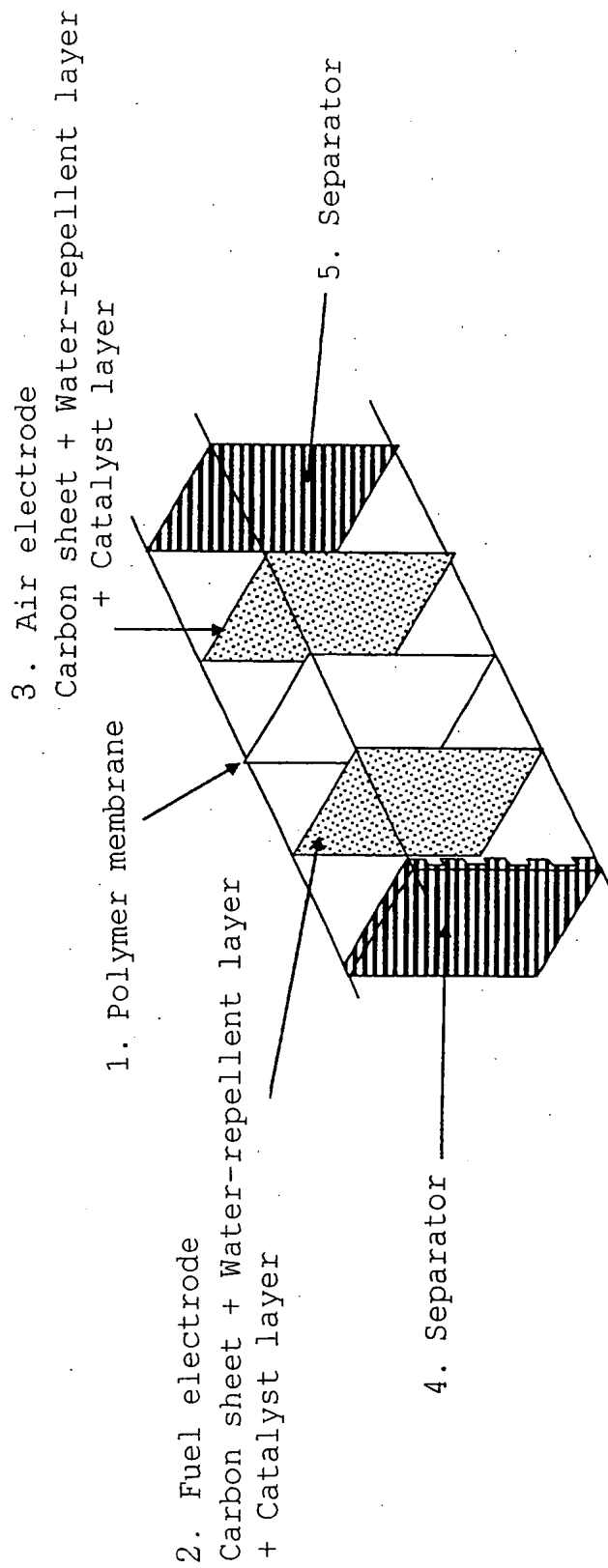
An electrode 2, 3 wherein the volume resistivity of the catalyst layer produced by spreading and drying a catalyst paste is not greater than $100 (\Omega \cdot \text{cm})$, and the ratio of the volume resistivity of said catalyst layer to the volume resistivity of said gas diffusion layer (volume resistivity of catalyst/volume resistivity of gas diffusion layer) is not greater than 10^7 , and the method of producing the electrode.

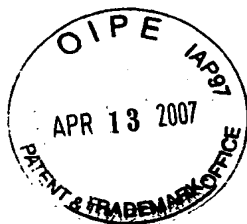
[Selected drawing] Fig. 1

[FIG. 1]

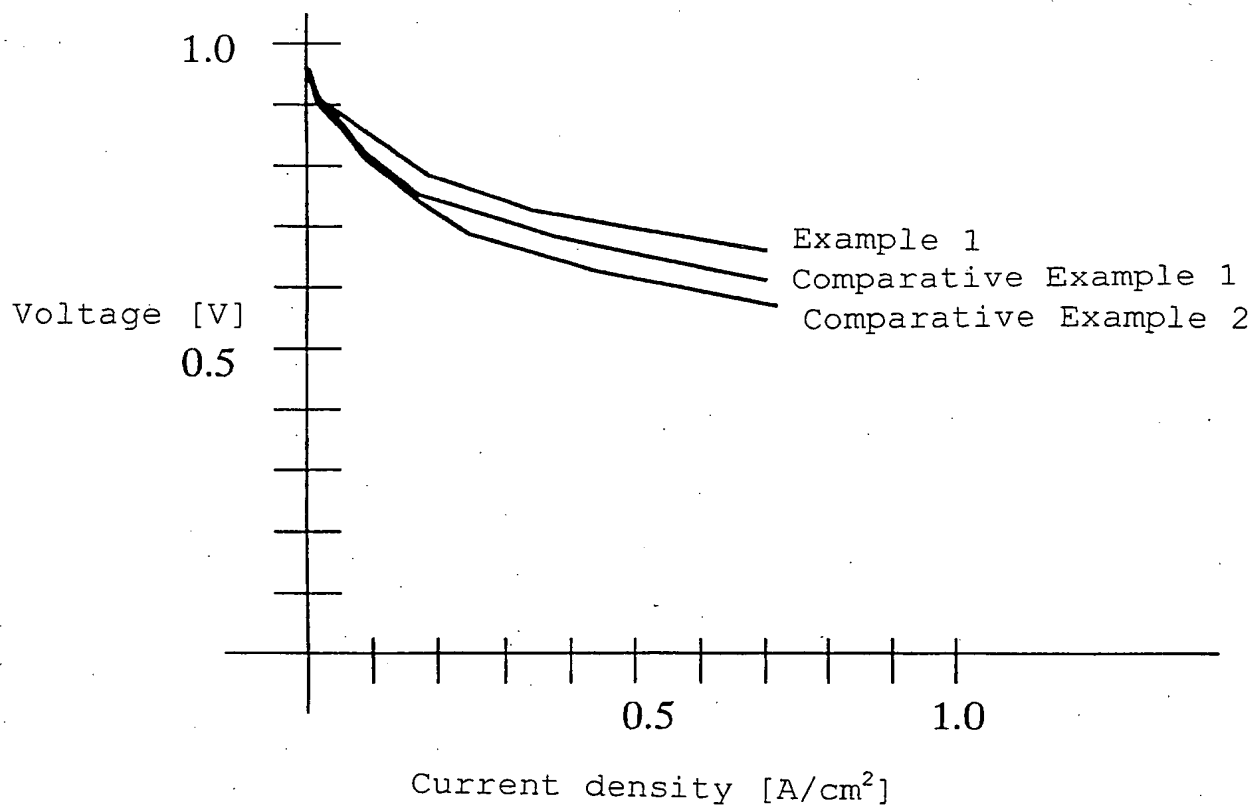
Electrode: Gas diffusion layer - Fuel electrode - Polymer membrane
- Gas diffusion layer

Single cell: Separator - Gas diffusion layer - Fuel electrode - Polymer membrane
- Air electrode - Gas diffusion layer - Separator





[FIG. 2]





[FIG. 3]

